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CHARACTERIZATION OF ANNEALED PULSED LASER DEPOSITED (PLD) THIN FILMS OF CESIUM OXYTHIOMOLYBDATE (Cs$_2$MoOS$_3$)

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14. ABSTRACT
Cesium oxythiomolybdate (Cs_2MoOS_3) is under consideration as a high temperature solid lubricant for silicon nitride bearings. However, Cs_2MoOS_3 oxidizes below the proposed maximum use temperature of 800 °C, and the oxidation process is complex. In the presence of silicon nitride, the oxidation reactions change. The purpose of the present research was to determine the chemistry of Cs_2MoOS_3 coatings grown by pulsed laser deposition (PLD) on several substrates (Si_3N_4, SiC, Inconel, Al_2O_3 and ZrO_2), and to determine the changes in chemistry and crystal structure after annealing in air to temperatures up to 800 °C. Many of the oxidation products identified are expected to be lubricious at elevated temperatures.

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Characterization of annealed pulsed laser deposited (PLD) thin films of cesium oxythiomolybdate (Cs$_2$MoOS$_3$)

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Abstract

Cesium oxythiomolybdate (Cs$_2$MoOS$_3$) is under consideration as a high temperature solid lubricant for silicon nitride bearings. However, Cs$_2$MoOS$_3$ oxidizes below the proposed maximum use temperature of 800 °C, and the oxidation process is complex. In the presence of silicon nitride, the oxidation reactions change. The purpose of the present research was to determine the chemistry of Cs$_2$MoOS$_3$ coatings grown by pulsed laser deposition (PLD) on several substrates (Si$_3$N$_4$, SiC, Inconel, Al$_2$O$_3$ and ZrO$_2$), and to determine the changes in chemistry and crystal structure after annealing in air to temperatures up to 800 °C. Many of the oxidation products identified are expected to be lubricious at elevated temperatures. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cesium oxythiomolybdate (Cs$_2$MoOS$_3$); Tribology; X-Ray diffraction (XRD); X-Ray photoelectron spectroscopy (XPS)

1. Introduction

Cesium oxythiomolybdate (Cs$_2$MoOS$_3$) is under consideration as a high temperature solid lubricant for silicon nitride bearings. King and Asmerom were the first to use Cs$_2$MoOS$_3$ as a lubricant [1], and noted that Cs$_2$MoOS$_3$ changes color from its original bright red-orange to a white powder during high temperature testing, indicating a change in chemical composition. Strong et al. [2] previously showed that oxidation of Cs$_2$MoOS$_3$ is complex, leading to a variety of products in the desired application range of 400–800 °C including: Cs$_2$SO$_4$, which further decomposes to cesium oxides and SO$_x$ gas; Cs$_2$MoO$_4$ and other complex cesium molybdates; and MoO$_3$.

The Cs$_2$MoOS$_3$ powder from Desilube, which was used in this study, did not have the stoichiometry and crystal structure described in the literature [2–5]. It was sulfur-deficient, and consisted of approximately 1/2 Cs$_2$MoOS$_3$, 1/4 Cs$_2$SO$_4$, and the remainder was cesium molybdates, molybdenum oxides, and MoS$_2$. In addition,

thermogravimetric analysis and Fourier transform infrared spectroscopy (FT-IR) revealed that Cs$_2$MoOS$_3$ is slightly hygroscopic [2].

King and Forester suggested that there may be interaction between Cs$_2$MoOS$_3$ and silicon nitride substrates [6]. To explore this possibility, Strong et al. heated Si$_3$N$_4$ and Cs$_2$MoOS$_3$ powders together in air, and analyzed the oxidation products [7]. When heated between 600 and 800 °C in the presence of silicon nitride, many oxidation products formed were the same as for pure Cs$_2$MoOS$_3$ powder. However, cesium oxides were not detected, and a significant amount of Cs$_2$MoO$_4$ was found. Most importantly, there was strong evidence that oxidation of the Si$_3$N$_4$ to amorphous SiO$_2$ in the presence of the alkali cesium ions led to the formation of a cesium silicate glass.

Cesium oxythiomolybdate-based lubricants have been applied by burnishing, mixing in greases, continuous powder feeding, and matrix binding [8]. However, these deposition methods have not proven optimal to prevent failure and ensure long wear life. Burnished powders and applied greases need to be replenished often. Continuously supplied powders require a supply system and consume a significant amount of powder over time.

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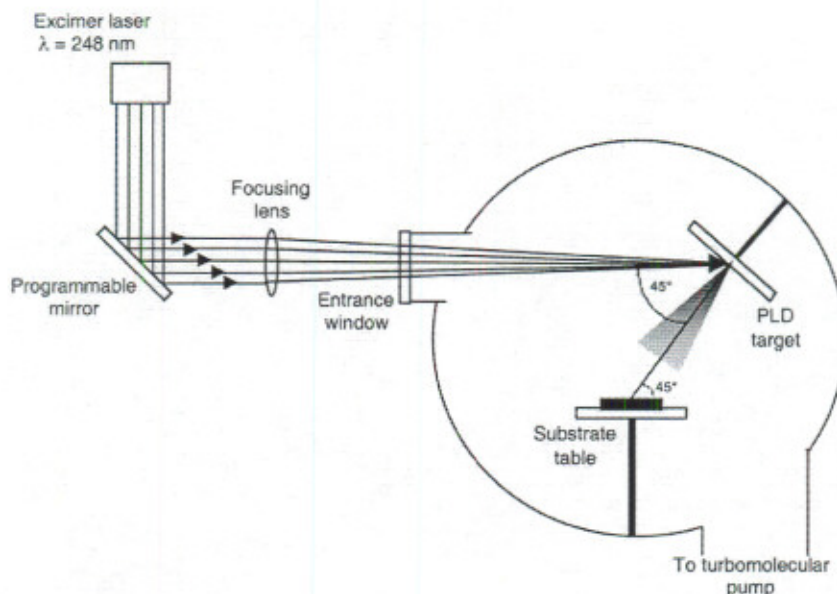*E-mail address:* karla.strong@wpafb.af.mil (K.L. Strong).

Fig. 1. Pulsed laser deposition (PLD) system.

Bonded coatings may exhibit poor adhesion to the substrate. A method of depositing Cs_2MoOS_3 coatings with precise thickness, good adhesion, and lubricious chemistry was desired.

Pulsed laser deposition (PLD) is an excellent method of depositing tribological films, and these films often exhibit superior tribological performance when compared to films deposited by other methods [9]. PLD was chosen as the deposition method for Cs_2MoOS_3 in this study primarily due to its characteristic of replicating the target chemistry in the film. Using PLD to grow films was expected to simplify identification of the compounds before and after annealing. In addition, the thickness of PLD films can be controlled from a few nanometers to as much as several micrometers. Also, PLD has been found to deposit highly adherent films. However, pulsed laser deposited solid films are thin, and are not suited to long-term use. Instead, PLD films are most advantageously employed for short-duration, one-time applications.

The purpose of the present research was to determine the chemistry of Cs_2MoOS_3 coatings grown by PLD, and to determine the changes in chemistry after annealing in air to temperatures as high as 800 °C. Silicon nitride and SiC were used to explore the possible formation of a cesium glass lubricant on the surface of silicon-containing substrates. Alumina (Al_2O_3), zirconia (ZrO_2), and inconel were selected to determine if other lubricious oxidation products (e.g. Cs_2SO_4, Cs_2MoO_4 and MoO_3) formed when the films were annealed. Analysis concentrated on the Cs_2MoOS_3/Si_3N_4 system, since silicon nitride has excellent properties for bearing applications at elevated temperatures [10]. Understand-

ing the thermal chemistry of the film is important to elucidate the lubrication mechanism in engineering applications.

2. Experimental details

2.1. Pulsed laser deposition

Cesium oxythiomolybdate powder obtained from the Desilube Corporation was cold pressed into 2.54 cm diameter targets for pulsed laser deposition. Other powders used as standards (Si_3N_4, Cs_2MoO_4, MoO_3, Cs_2SO_4, Cs_2SiO_3 and MoS_2) were obtained from Alfa–Aesar, and were reported as 99.95% pure. Polycrystalline β-Si_3N_4 and SiC substrates were obtained from International Ceramics Engineering and Insaco, respectively, and were 99.9% pure polycrystalline materials. Inconel alloy 718 was employed as one substrate. The oxide substrates were also polycrystalline and 99.9% pure. All substrates were polished to a 1-μm finish. Silica interfaces were crystalline thin films (25 nm) grown on silicon wafers and were obtained from Process Specialties. These substrates had a surface finish much smoother than 1 μm, typical for the electronics industry.

A Lambda Physik KrF excimer laser produced light at a wavelength of 248 nm, which was delivered to the PLD chamber. A diagram of the system is shown in Fig. 1. The laser light reflected off of a programmable mirror which rastered the beam across the target in two dimensions, in order to evenly remove material from the surface and to minimize pitting. The beam then passed through a focusing lens and a magnesium fluoride

window, which transmitted 93% of the beam's intensity. The laser beam struck the target at a 45° angle, and the substrate was positioned along the target normal at a distance of 10.8 cm at an angle of 45° to the target normal. The target and substrate were rotated during deposition to optimize coating uniformity. The beam was focused to a rectangular spot (5.7×1.85 mm) as it hit the target. The target and substrate were contained in a vacuum chamber with a pressure of 5×10^{-7} torr or less. All films were grown using 300 mJ/pulse, and a repetition rate of 20 Hz. The energy density was approximately 2.5 J/cm^2 at the target surface (power density $\sim 1 \times 10^8$ W/cm^2). The laser pulse duration was 20 ns. The laser, rastering mirror, and deposition time were controlled by computer to ensure reproducibility. Additional details of the pulsed laser deposition system have been described previously [11].

Before deposition, substrates were ultrasonically cleaned in acetone for 10 min and methanol for 3 min. After positioning in the deposition chamber, the substrates were cleaned by argon ion sputtering with a Kauffman source for 10 min. Cs_2MoOS_3 films were deposited on Si_3N_4, SiC, Inconel, Al_2O_3 and ZrO_2 substrates at room temperature. The Cs_2MoOS_3 films were nominally 1 μm thick, and required approximately 15 min to grow. Thin Cs_2MoOS_3 films (150 nm) were grown on a Si_3N_4 substrate in order to use X-ray photoelectron spectroscopy (XPS) and XPS depth profiling to study the interfacial chemical composition of the films after annealing in air.

To detect the background gas species generated during PLD, Cs_2MoOS_3 was laser ablated in the presence of a Farran Scientific Micropole quadrapole mass spectrometer. The spectrometer had a mass range of 2–65 amu. The PLD system used in this experiment was employed at an energy density of approximately 2 J/cm^2. The repetition rate was 20 Hz. The background pressure was 6×10^{-7} torr. The mass spectrometer was located 33 cm from the target at approximately 45° from the target normal. A plate was installed 2 cm in front of the mass spectrometer head such that the line-of-sight between the target and the mass spectrometer was completely masked. Therefore, only background and scattered gases were detected.

Films deposited on Si_3N_4 were annealed at 300, 600 and 800 °C in air. Films deposited on other substrates were annealed at 600 °C. The films were annealed for 6 h.

2.2. Film characterization

After annealing, films were analyzed by scanning electron microscopy (SEM), XPS, X-ray diffraction (XRD), and Raman spectroscopy, to detect changes in chemical composition and crystal structure with annealing temperature. Scanning electron microscopy was performed on a LEICA 360 Field Emission scanning electron microscope. The samples were coated with a few nanometers of gold–palladium for charge neutralization.

X-Ray photoelectron spectroscopy was performed in a Surface Science Instruments M-probe XPS instrument operated at a base pressure of $<1 \times 10^{-9}$ torr. Using an Al anode, a 400×1000 μm line spot, and 25 eV pass energy, the full width at half maximum of the Au 4f$_{7/2}$ peak was 0.85 eV. Binding energy positions were calibrated against the Au 4f$_{7/2}$ peak, and energy separations were calibrated using the Cu 3s and Cu 2p$_{3/2}$ peaks at 122.39 and 932.47 eV, respectively. The full width at half maximum of the Au 4f$_{7/2}$ peak was 0.71 eV, and the detection limit was less than 2.0%. Peak fitting was performed to calculate chemical composition. Samples were typically sputtered for 1 min prior to analysis to remove surface carbon and oxygen. Samples were insulating, so an electron flood gun was used for charge neutralization.

A Rigaku D/max-B diffractometer equipped with a thin film attachment and a monochromator was used to perform X-ray diffraction. Chemical phase identification was performed using a computer-based system with the standard Powder Diffraction File (PDF) library [5] embedded in it. Glancing angle XRD was taken at an angle of 2–3° with the substrate surface to enhance the signal from the film.

Micro-Raman spectroscopy was performed with a Renishaw Raman microscope, and laser light at 514.5 nm from an Ar$^+$ laser was used in the analyses. Calibration was performed with the Si peak at 520.7 cm^{-1}. In some cases, Raman spectroscopy was performed on a SPEX 1877 0.6 m triple spectrometer. The results from the two instruments are directly comparable when the data are normalized.

3. Results

3.1. SEM analysis of PLD films

Cs_2MoOS_3 films appeared uniform by visual inspection upon removal from the PLD chamber. After aging in laboratory air for several hours, the films became mottled; films stored in vacuum remained uniform. Fig. 2 shows SEM micrographs of as-deposited (a,b) and aged (c,d) films deposited on Si_3N_4. Upon closer inspection at high magnification (b,d), it is apparent that both films have bumps, cracks, and tiny holes, but the as-deposited films are smoother than the aged films. The aged films also have small white areas, which are approximately 250 μm long and 50 μm wide. Since Cs_2MoOS_3 is hygroscopic [2], mottling may be caused by hydration of the film surface. Fig. 2 also shows SEM micrographs of a film after annealing to 600 °C (e,f). It is also rough, and has white areas (approx. 500×100
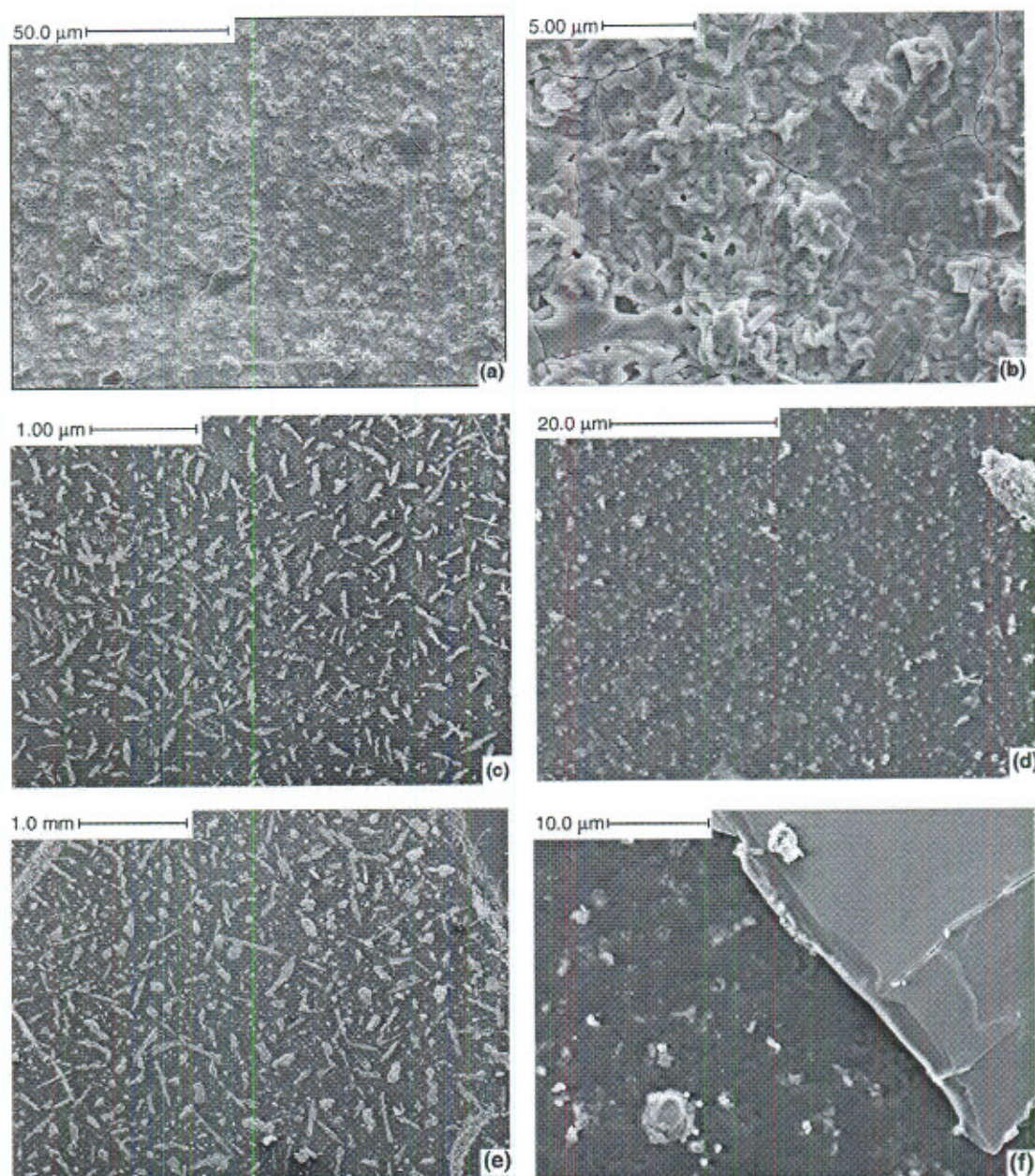
Fig. 2. SEM micrographs of Cs_2MoOS_3 film: (a,b) as-deposited on Si_3N_4; (c,d) deposited on Si_3N_4 and aged in ambient air; and (e,f) deposited on Si_3N_4 and annealed at 600 °C in air.

μm) evenly distributed across the surface. Auger electron spectroscopy sampling an area of 50×50 μm, confirmed no significant difference in the chemical compositions of the dark and white areas.

3.2. Mass spectroscopy

The background gases present in the chamber before ablating the target were primarily water vapor and carbon dioxide. Species at 28, 32, 48 and 64 amu appeared during laser ablation of Cs_2MoOS_3, as shown

in Fig. 3. The most important observation was that sulfur was contained in the background gas and was likely to be pumped away, leading to a sulfur deficiency in the resulting films. Masses appearing at 32 amu (S), 48 (SO), and 64 (S_2) support this conclusion.

3.3. XPS analysis

XPS was used to determine film stoichiometry. Carbon and oxygen were present as surface contamination, but were almost entirely removed with sputter etching.
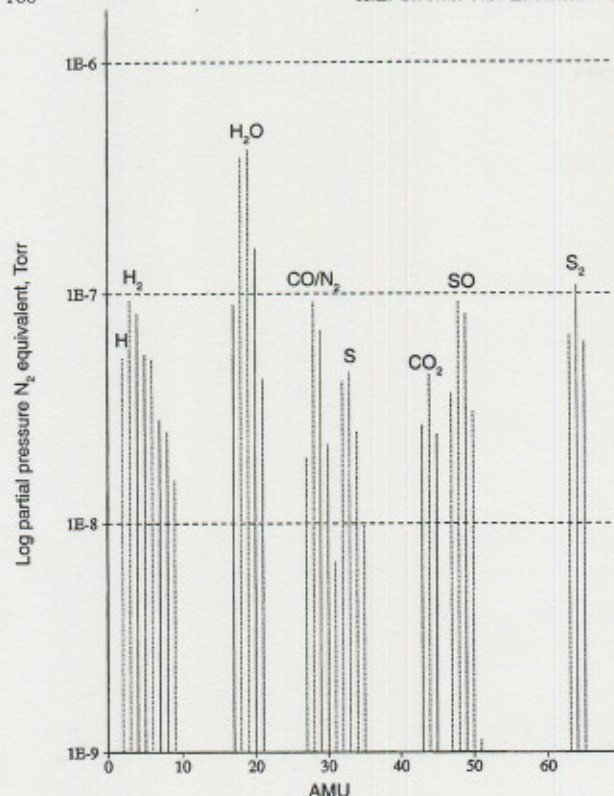
Fig. 3. Mass spectrogram of background gases in deposition chamber during laser ablation of Cs_2MoOS_3.

Any remaining carbon on the surface was not considered in the analysis. All the oxygen was included in the analysis, as it is difficult to differentiate O contamination from oxygen contained in Cs_2MoOS_3 or the oxide substrates.

Determining the atomic concentrations of N, Mo and S was difficult due to peak overlap. The Mo $3d_{3/2}$ and $3d_{5/2}$ peaks (230 and 227 eV) nearly overlap the Cs 4s peak (231 eV) and the S 2s peak (229 eV). Also, the S 2p peaks at 164/165 eV are between the Cs $4p_{3/2}$ and $4p_{1/2}$ peaks at 162 and 172 eV, respectively. The S 2p peaks were chosen for analysis. Peaks were deconvoluted by constraining the Cs peaks to remain 10 eV apart. The N 1s peak at 399 eV is close to the Mo $2p_{3/2}$ peak at 393 eV, complicating the analysis of N and Mo. The Mo $3p_{1/2}$ peak at 410 eV was selected for analysis. Peak shifting, broadening, and asymmetry toward lower binding energy were common due to sample charging and charge neutralization with the electron flood gun. The X-ray spot was larger than the white areas on the films, so that only an average surface composition was measured.

Chemical composition of the 1-μm thick Cs_2MoOS_3 films deposited on each substrate, and changes in composition with annealing temperature are shown in Table 1. As-grown films were deficient in S and Mo, and rich in O when compared to the starting powder. In general,

as the annealing temperature increased, the percentages of Cs, Mo and S decreased, and that of O increased, indicating oxidation. Sulfur was not detected on samples heated above room temperature except in films deposited on Inconel, which also had high room temperature concentrations of sulfur.

For films deposited on Si_3N_4, Si and N were evident even before heating, which is consistent with the presence of cracks and holes as seen in Fig. 2. The presence of these defects may indicate poor film adhesion to the substrate or excessive film stress at room temperature. As stated above, N was difficult to detect, and the values in Table 1 reflect that uncertainty. When these films were heated to 300 °C, the percentage of Cs increased and that of O decreased, contrary to the general results. This may have been due to the formation, melting, and spreading of cesium oxides on the film surface, preventing detection of the underlying elements. This trend would be expected if the cesium oxides, such as Cs_2O_2 or Cs_2O, had a higher concentration of Cs and a lower concentration of O than the underlying film. Most cesium oxides melt between 400 and 600 °C [12].

At annealing temperatures of 600 and 800 °C, the sample surfaces contained primarily Si and O, with small amounts of Cs and Mo. The general oxidation trend resumed (i.e. the O concentration increased), indicating that the cesium oxides were no longer concentrated at the surface. Between 600 and 800 °C, there was a sharp decrease in the amount of Mo. This would be expected if MoO_3 was formed in the annealed films. This compound sublimes at approximately 700 °C [13].

Table 1
Atomic percent composition of pulsed laser deposited Cs_2MoOS_3 film surfaces after annealing, as determined from XPS

| Substrate	Temperature (°C)	Atomic composition					
		Cs	Mo	O	S	Si	N
n/a	Calculated stoichiometric	28.6	14.3	14.3	42.9		
n/a	As-received powder	27.6	16.3	25.4	30.5		
Si_3N_4	25	26.5	8.0	47.1	4.1	12.0	2.3
Si_3N_4	300	35.7	7.5	39.8	0	17.0	0
Si_3N_4	600	13.8	4.4	70.1	0	19.7	0
Si_3N_4	800	6.1	0.2	64.5	0	28.2	0
SiC	25	38.0	1.4	52.1	8.5	0	
SiC	600	15.4	3.2	81.3	0	0	
Al_2O_3	25	30.5	6.7	56.8	6.1		
Al_2O_3	600	24.1	9.7	66.2	0		
ZrO_2	25	39.9	11.9	48.2	0		
ZrO_2	600	15.3	13.5	71.2	0		
Inconel	25	33.6	11.0	41.6	13.8		
Inconel	600	17.8	2.7	77.6	1.9		
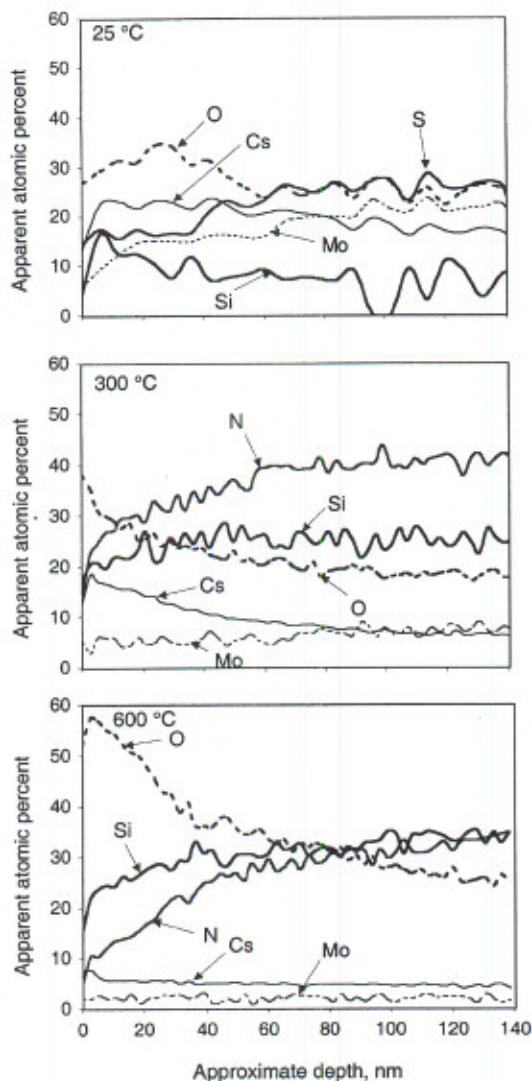
Fig. 4. XPS depth profiles, Cs_2MoOS_3 deposited on Si_3N_4, 1 µm films.

3.4. XPS depth profiles of Cs_2MoOS_3 PLD thin films

XPS depth profiles were performed on 1 µm thick films grown on Si_3N_4 as-deposited and after annealing at 300 and 600 °C to determine subsurface stoichiometry. These depth profiles are shown in Fig. 4. The composition of the film at 25 °C was nearly constant to a depth of 140 nm. Films annealed at 300 and 600 °C both showed a decrease in Cs and O and an increase in Si and N with depth, implying interdiffusion between the film and the substrate. No S was detected in the annealed films to a depth of 140 nm.

A 150 nm thick film grown on Si_3N_4 was depth profiled to monitor changes in the chemical composition at the film/substrate interface with annealing temperature. Analysis was performed immediately following

film growth, after aging in ambient air for several weeks, and after annealing to 600 and 800 °C. Depth profiles are shown in Fig. 5. The as-deposited and aged films were assessed to determine the effect of hydration on the film chemical composition. The depth profiles of the two films were identical. The composition of these films was constant to an approximate depth of 150 nm. At that point, an abrupt interface was detected, where the concentrations of Cs and O dropped below 10%, and the concentration of Si was approximately 90%. Nitrogen was not differentiable from Mo, so neither was plotted in Fig. 5 for the room temperature film. Peak shifting, indicating a change of chemical state, was not detected except in O in the top 5 nm of the film, where the peak shifted from 531.1 to 529.6 eV, indicating that the O detected at the surface was contamination (H_2O, CO_2 or O_2). The subsurface O was contained in oxides and/or sulfates. The shift was apparent in both aged and as-deposited films, which is somewhat surprising,
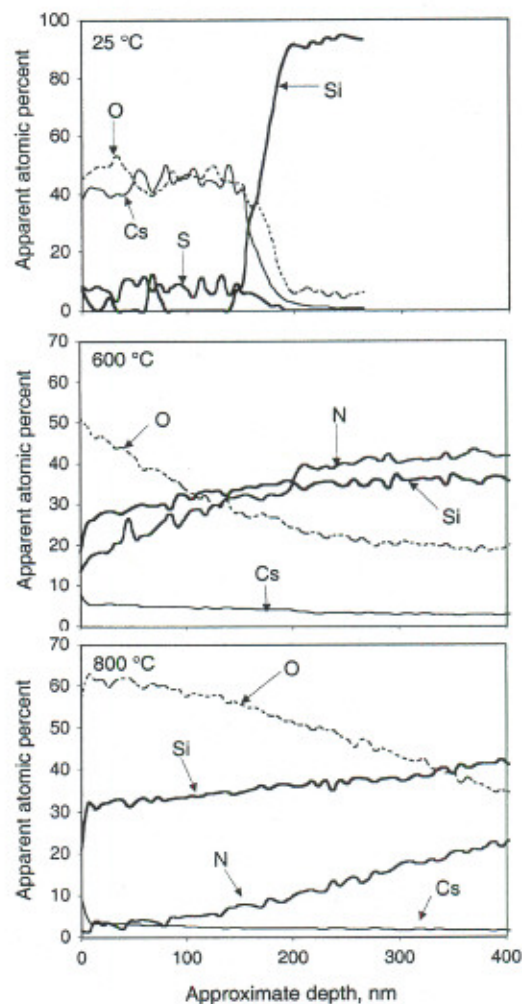

Fig. 5. XPS depth profiles, Cs_2MoOS_3 deposited on Si_3N_4, 150 nm films.
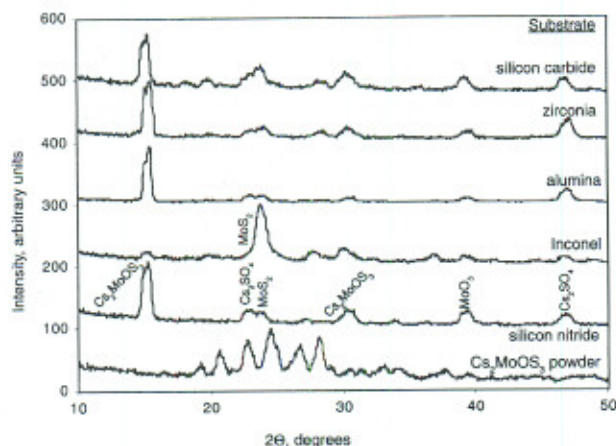
Fig. 6. XRD spectra of Cs_2MoOS_3 films as-deposited on several substrates.

since the as-deposited film had been exposed to ambient air for only a few minutes during transfer to the XPS chamber. It is apparent that Cs_2MoOS_3 reacts with water and/or oxygen quickly when exposed to the atmosphere.

After annealing at 600 and 800 °C, S and Mo were undetectable in the 150 nm films. The amount of O greatly increased in the films and into the substrate. The amount of Cs at the surface decreased. After annealing, 3–5 at.% Cs was found at a depth greater than 400 nm, much deeper than the original film thickness. It was not likely that the ion sputtering caused 'knock in' of the Cs (driving the Cs into the substrate), since this phenomenon was not observed in the as-deposited films. An interface was no longer distinguishable at either temperature. The film annealed at 600 °C was primarily silica to a depth of 50 nm, and when annealed at 800 °C, the silica layer was at least 200 nm thick.

One explanation for the appearance of a gradual interface might be the 'pooling' of the film material on the surface of the substrate during heating, forming discontinuous islands of film. Since the XPS sample size is large, it is possible that the signal detected reflected an average of the islands of film and the exposed substrate. As more of the film was sputtered away, the results would indicate a gradual transition from the film composition to that of the substrate, just as was observed in this case. However, the SEM evidence does not support this explanation. Islands are not formed, so interdiffusion between the film and the substrate is the likely explanation for the observed compositional variation with sputter depth.

3.5. XRD analysis

XRD of as-deposited Cs_2MoOS_3 films revealed that the crystal structure was different from that of the parent material, and also different from the powder diffraction

file (PDF) standard for Cs_2MoOS_3 [5]. These results are shown in Fig. 6. Peaks due to Cs_2MoOS_3, MoS_2, MoO_3 and Cs_2SO_4 were identified. The crystal structure of these films was nearly identical on every substrate except Inconel. As shown in Fig. 6, the film deposited on Inconel had a significant MoS_2 peak. This result was consistent with the higher concentration of sulfur identified in these films with XPS.

As the films were annealed in air to progressively higher temperatures, the film structure changed significantly. Fig. 7 compares films deposited on Si_3N_4 and annealed, and also shows the peaks of the PDF standard for Si_3N_4. It was difficult to identify specific phases from these spectra due to the large number of possible oxidation products; therefore, the peak assignments may not be unique. The film annealed to 300 °C contained Cs_2SO_4. The primary compounds identified at 600 °C were cesium oxides, molybdenum oxides, and Cs_2MoO_4; Cs_2SO_4 was no longer apparent. Crystalline SiO_2 (cristobalite) was identified in the sample heated to 800 °C.

The spectra of the films deposited on each of the substrates and annealed at 600 °C are compared in Fig. 8. While each spectrum appears to be unique, they are actually quite similar. Most of the differences can be attributed to peaks associated with the various substrates. In each spectrum, cesium oxides, molybdenum oxides (including MoO_3), and cesium molybdates (including Cs_2MoO_4) were identified. However, the peak intensities for these compounds varied.

3.6. Raman analysis

Raman spectra for Cs_2MoOS_3 films grown on Si_3N_4 and annealed in air are shown in Fig. 9. Raman confirmed that the crystal structure of the parent material
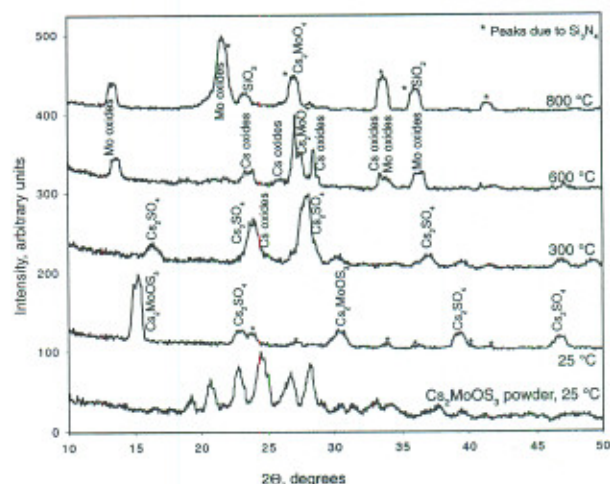

Fig. 7. XRD spectra of Cs_2MoOS_3 films deposited on Si_3N_4, annealed in air.
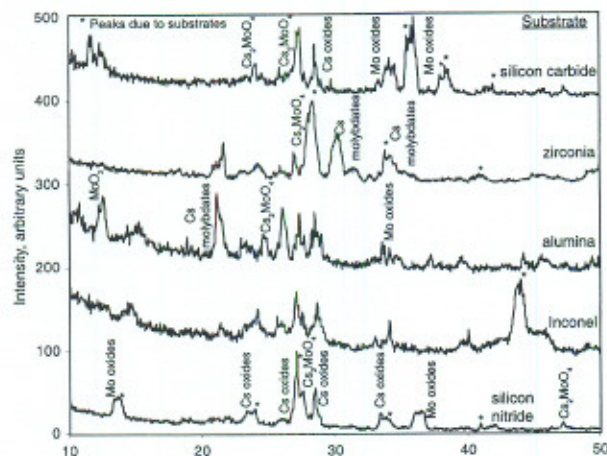
Fig. 8. XRD spectra of Cs_2MoOS_3 deposited on several substrates, annealed at 600 °C in air.

and the room temperature films were dissimilar. The spectra were compared to standards of Si_3N_4, Cs_2MoO_4, MoO_3, Cs_2SO_4, Cs_2SiO_3, MoS_2, and the literature [14]. None identically matched the films. In spectra for the as-deposited film and the film annealed at 300 °C, the large peaks at 463 and 473 cm^{-1} are characteristic of pulsed laser deposited Cs_2MoOS_3 films. The other compounds identified in the film annealed at 300 °C were Cs_2MoO_4, MoS_2 and MoO_3. There was a strong indication of Cs_2MoO_4 in the film annealed at 600 °C, as was seen in XRD. The unidentified peaks in the 600 and 800 °C spectra are likely associated with cesium oxides, molybdenum oxides, and cesium molybdates for which standards and literature data were unavailable, but which were identified in XRD.

Raman spectra of Cs_2MoOS_3 films as-deposited on other substrates (Al_2O_3, ZrO_2, SiC and Inconel — not shown) confirm the XRD results. The films were nearly identical to those deposited on Si_3N_4 except the film deposited on Inconel, which had two major peaks at 377 and 477 cm^{-1} due to MoS_2 [14]. At 600 °C, the films changed significantly. Each spectrum exhibited peaks due to the underlying substrates, along with those of MoO_3, Cs_2MoO_4 and other oxides, with differing intensities.

4. Discussion

This study has shown that pulsed laser deposition can be used to deposit thin films of Cs_2MoOS_3 on a variety of substrates. They were partially crystalline, and had a different stoichiometry and crystal structure from both the published data for Cs_2MoOS_3 and the parent material produced by the Desilube Corporation. The chemical composition of the films was sulfur-deficient and oxygen-rich. The sulfur deficiency was consistent with the mass spectrometry results and the low sulfur content of

the as-received Cs_2MoOS_3 powder. The increase in oxygen is probably due to reaction of the film with water and possibly CO_2 and O_2 when exposed to air. Cesium oxythiomolybdate, Cs_2SO_4, MoS_2 and MoO_3 were present in the as-deposited films.

The crystal structure of as-deposited films was the same regardless of the substrate material, with the exception of the films deposited on Inconel. In these films, MoS_2 was produced preferentially over Cs_2MoOS_3 or Cs_2SO_4. This was evident from Raman and XRD results. The cause of the difference in films deposited on Inconel is unknown, but it may be related to its metal content.

During heating, Cs_2MoOS_3 deposited on substrates containing no silicon went through the same oxidation reactions as previously found for Cs_2MoOS_3 powder [2]. Oxidation begins at approximately 400 °C. Between 400 and 600 °C, Cs_2MoOS_3 oxidized to Cs_2SO_4, which further oxidized to cesium oxides and SO_x gas. Cesium molybdates (including Cs_2MoO_4), and molybdenum oxides (including MoO_3) were also formed.

When Cs_2MoOS_3 was deposited on Si_3N_4 and SiC substrates, many of the same oxidation products were identified after annealing at 600 °C. In addition, films deposited on Si_3N_4 and annealed to 800 °C were composed primarily of Si and O, with a few percent Cs, as shown by XPS. X-Ray diffraction revealed cristobalite in these films. The presence of crystalline SiO_2 indicates that at shorter times or at lower temperatures, glassy SiO_2 existed.

The mechanism for glass formation may be as follows: near 700 °C, Si_3N_4 is known to oxidize to amorphous SiO_2 [15,16]. At that point, cesium ions from melted cesium oxides on the surface diffused into the SiO_2, likely forming a cesium silicate glass. This
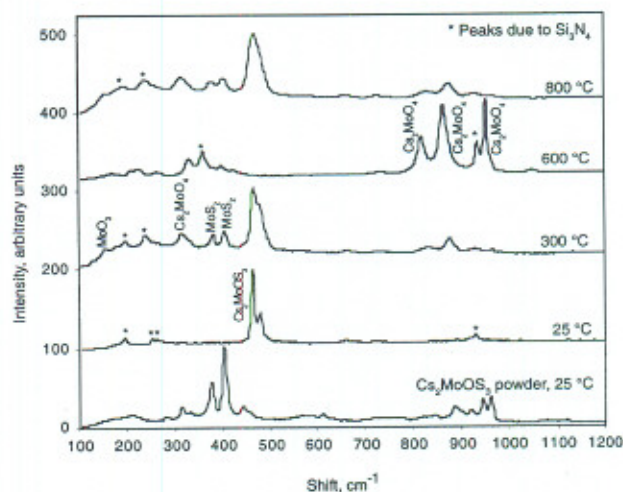

Fig. 9. Raman spectra of Cs_2MoOS_3 deposited on Si_3N_4, annealed in air.

accounts for the decrease in the percentage of Cs detected with XPS at 600 °C and above. It has been found previously with differential scanning calorimetry (in combination with other techniques) that mixtures of Cs_2MoOS_3 and Si_3N_4 powders formed a glass at approximately 700 °C, which devitrified (crystallized) at approximately 825 °C [7]. While the role of sulfur in lubricious Cs_2MoOS_3 has been debated [1,6,8,17], in the present study it was found to be crucial. The oxidation route proposed above requires the presence of sulfur in order to produce cesium oxides and subsequently, cesium silicate glass [18].

The presence of the particular oxidation products identified is significant for tribological applications. Molybdenum disulfide is a well-known lubricant, which is useful up to approximately 350 °C [13]. All of the compounds detected at 600 °C are likely to have shear strength low enough at that temperature to be lubricious. For example, molybdates and MoO_3 have low coefficients of friction near 600 °C [13,19,20]. Cesium sulfate and cesium oxides may act as lubricants between their formation temperature and decomposition or melting temperatures (approx. 300–600 °C) [21]. Also, pulsed laser deposited sulfates have been shown to have low friction at 600 °C [22].

The cesium silicate glass which was indicated in the Si_3N_4 system is also likely to be lubricious at elevated temperature. Alkali ions are known to reduce the viscosity of silicate glasses [23], which would reduce the shear strength at a given temperature, and increase the lubricity of the glass. In fact, glasses have been used as lubricants for steel working for over 50 years [24]. Together, the combination of several compounds with different melting points may extend the lubricious range of Cs_2MoOS_3 from approximately 300 to approximately 800 °C.

The formation of a low shear strength glass has previously been postulated as the lubrication mechanism for cesium tungstate (Cs_2WOS_3) bonded coatings (containing Na_2SiO_3) on silicon nitride bearings by Rosado et al. [17]. Cesium tungstate is comparable to Cs_2MoOS_3, where W is substituted for Mo in the crystalline lattice. In Rosado's study, it was thought that at elevated temperature, Cs_2WOS_3 decomposed to Cs_2O (m.p.$=495$ °C) [21] and SO_3 gas. The cesium ions from the melted cesium oxide were reported to react with the silicate in the coating to form the lubricating film at elevated temperature. In the present case, the silicate binder is not required to form a cesium silicate glass from Cs_2MoOS_3 films deposited on Si_3N_4 substrates.

To fully understand the XPS depth profile results, an understanding of the film microstructure as revealed by SEM is helpful. In as-deposited films, nucleation of film growth appeared to be random, followed by growth in a dendritic structure until the dendrites grew into each

other. As the film cooled from the deposition temperature, which was slightly elevated due to the impingement of the film ions, the film cracked. This growth mechanism results in small holes and cracks in the film at room temperature, which would allow the detection of the substrate with XPS. As the films were annealed, the film appears to diffuse across the substrate, 'healing' the cracks and holes. These features are no longer evident in annealed films. There is no evidence that the film material 'pools' into island-like structures.

The XPS depth profiles can then be interpreted as representative of a gradual interface between the film and the substrate. The gradual interface eliminates the possibility of adhesive film failure. Also, during rubbing, as small amounts of film are worn away, cesium, which diffused deeply into the substrate, would continue to be available to reduce the viscosity of a continuously forming silicate glass, creating a 'self healing' film. Clearly, pulsed laser deposited Cs_2MoOS_3 films have the potential to be excellent lubricants on silicon-containing substrates, and may perform well at elevated temperatures on a variety of substrates.

5. Conclusions

The purpose of the present research was to determine the chemistry of Cs_2MoOS_3 coatings grown by PLD, and to determine the changes in chemistry and morphology after annealing in air to temperatures as high as 800 °C. The primary conclusions drawn from this study were:

1. As-deposited films of Cs_2MoOS_3 were moderately rough and cracked, and were not pure crystalline Cs_2MoOS_3. They were partially crystalline, containing Cs_2MoOS_3, Cs_2SO_4, MoS_2 and MoO_3. The latter three of these compounds may be lubricious at room temperature (MoS_2) or elevated temperature (Cs_2SO_4 and MoO_3). The films were likely hygroscopic, which may affect performance below 100 °C. Films deposited on Inconel substrates contained more MoS_2 than films deposited on other substrates.

2. When annealed, films oxidized to primarily Cs_2SO_4 at 300 °C, which decomposed to cesium oxides and SO_x below 600 °C. Also present at 600°C were cesium molybdates (including Cs_2MoO_4), cesium oxides, and molybdenum oxides (including MoO_3). All of the solid compounds may be lubricious at elevated temperatures.

3. Films deposited on Si_3N_4 and annealed to 800 °C also contained crystalline SiO_2, which indicated the presence of amorphous silicate glass at lower temperatures or when heated for shorter times. The combination of silicate glass and melted cesium oxides at temperatures between 400 and 800 °C is likely to create a cesium silicate glass as the cesium ions

diffuse into the oxide. This glass may be lubricious at elevated temperatures.

4. Annealing films deposited on Si_3N_4 to 600 °C or above caused the diffusion of cesium into the substrate, eliminating the sharp interface between the film and the substrate. This implies that the film will have good adhesion at elevated temperature. Cesium was found very deep in the substrate, indicating that the formation of a cesium silicate glass surface may occur continuously during wear, which would provide a 'self healing' film.

5. Because each of the compounds formed by the decomposition of Cs_2MoOS_3 films has a different temperature range over which it is lubricious, these compounds may provide continuous lubrication from 300 to 800 °C. Pulsed laser deposited Cs_2MoOS_3 has good potential as a high temperature solid lubricant.

Acknowledgments

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